

# Monomer tailoring to control the redox potentials of conductive polyheterocycles

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Ring fusion of two terminal polymerogenic heterocycles (pyrrole or thiophene) onto a central [(hetero)aromatic] or carbocyclic ring strongly modifies, relative to pyrrole or thiophene, both the peak potentials of the monomer and the redox potential of the polymer. Conductivity, peak potentials and redox potentials of materials obtained by polymerization of pyrrolic and/or thiophene systems fused onto central benzene, cyclopentadiene, thiophene and pyrrole rings are reported. The approach can be exploited to beneficially design new polyheteroaromatics endowed with highly valued properties (good conductivities and environmental stability).

(Keywords: conductivity; redox system; heterocyclic monomers)

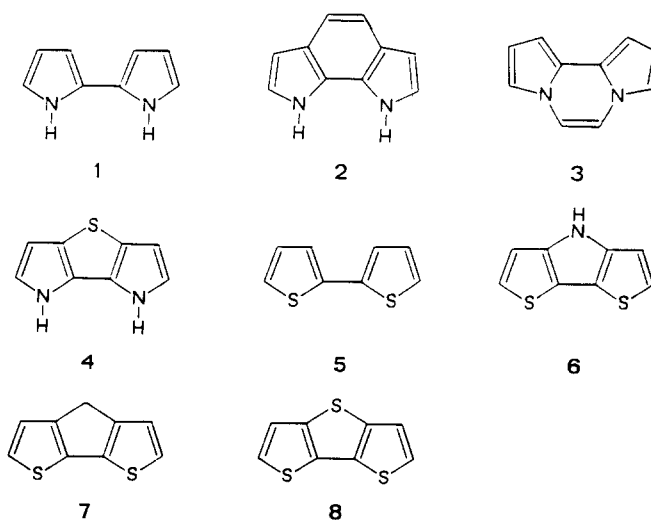
Neutral polypyrrole (PP) produced by cathodic reduction of the conductive polymer is an oxygen-sensitive material because of its negative oxidation potential ( $-0.20$  V versus SCE)<sup>1</sup>: its physical and spectroscopic characterization, although highly desirable, is therefore difficult. Conversely, oxidized polythiophene (PT) is a relatively strong oxidant ( $0.70$  V versus SCE)<sup>2</sup>: it can thus be reduced (dedoped) by several environmental agents. Indeed, for batteries based on PT and working with organic electrolytes, a 40% decay in discharge capacity is reported after only 50 h of storage in the charged state<sup>3</sup>. It is evident that for application purposes an increase of redox potentials of pyrrole-based polymers would be beneficial: the opposite is true for thiophene-based polymers.

Redox potentials can be varied by placing substituents on the rings: the electron-withdrawing substituents increase, while the electron-donating ones decrease, the redox potential of the parent system. However, since both pyrrole and thiophene undergo oxidative polymerization in the  $\alpha,\alpha'$ -positions, the only remaining positions available for introducing a substituent are *ortho* to the bond linking the two heterocyclic units: this may be detrimental for the planarity of the final polymer and thus for its conductivity.

We wish to report the general principle that redox potentials can be increased or decreased, according to specific needs, if in the starting monomer two pyrrole and/or thiophene rings are fused onto a central [(hetero)aromatic] or carbocyclic ring, designed to correctly modulate the  $\pi$  electronic distribution. We arrived at the definition of the principle following the 'spacer'

strategy<sup>4-6</sup> of functionalizing heterocycles at a position remote from the sites involved in the polymerization. Polymerization of selected monomers to new polymers provides data that support the principle.

With respect to 2,2'-dipyrrolyl (1), an ethylenic fragment bridging either positions 3,3' or the nitrogen atoms of 1 causes fusion of the pyrrole units onto a benzene or a pyrazine ring to form 1H,8H-pyrrole[3,2-*g*]indole (2) or dipyrrolo[1,2-*a*;2',1'-*c*]pyrazine (3). Similarly, a thioether fragment bridging positions 3,3' of 1 forms 4H,5H-thieno[3,2-*b*;4,5-*b'*]dipyrrole (4). Analogously, with respect to the 2,2'-dithienyl (5) an -NH- or a methylene or a thioether fragment bridging positions 3,3' causes the two thiophene units of 5 to be fused onto a pyrrole or a cyclopentadiene or a thiophene ring, to form, respectively, 4H-dithieno[3,2-*b*;2',3'-*d*]pyrrole (6),



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**Table 1** Oxidation peak potentials ( $E_{pa}$ ) of the monomers, polymer redox potentials ( $E^0$ ) and conductivity ( $\sigma$ ) data

Monomer	$E_{pa}$ (V) <sup>a</sup>	$E^0$ (V) <sup>a</sup>	$\sigma$ ( $\Omega^{-1} \text{ cm}^{-1}$ )
1	0.55	-0.20	100
2	0.74	0.49	5
3	0.56	0.40	0.2
4	0.42	-0.19	2
5	1.31	0.70	40
6	0.86	0.34	6
7	0.99	0.59	40
8	1.20	0.50	0.4

<sup>a</sup> Versus SCE

4H-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (7), or dithieno[3,2-*b*;2',3'-*d*]thiophene (8). We have polymerized electrochemically (acetonitrile, tetrabutylammonium perchlorate as supporting electrolyte) the substrates 2–4<sup>6–8</sup> and 6 and 7<sup>9,10</sup>. The oxidation potentials  $E_{pa}$  of the monomers, the redox potentials of the polymers  $E^0$ , and conductivities of the oxidized (doped) polymers are shown in Table 1. Data for systems 1, 5 and 8 are from the literature<sup>1,2,11,12</sup>.

It can be seen that fusion of dipyrrolyl 1 onto an electron-poor heterocycle such as pyrazine or onto a benzene ring increases both  $E_{pa}$  and  $E^0$ : although conductivities of the polymers of 2 and 3 are somewhat decreased, the loss is not dramatic. The important result is that, in contrast with PP, both the neutral polymers of 2 and 3 are stable to air. Instead, fusion of 1 onto a central electron-rich  $\pi$ -excessive thiophene ring, decreases the  $E_{pa}$  of the monomer 4 relative to 1, but does not affect appreciably the  $E^0$  of the polymer, which behaves as a PP.

Conversely, fusion of the dithienyl 5 onto central electron-rich  $\pi$ -excessive pyrrole, thiophene and even cyclopentadienyl rings, decreases, relative to the monomer 5, both  $E_{pa}$  and  $E^0$ : once again, conductivities are not importantly affected but are somewhat decreased.

Since oxidized, conductive polymers obtained from 6–8 will be dedoped with more difficulty than polythiophene, batteries employing such electrodes are expected to undergo more limited self-discharge.

In conclusion, we have shown the beneficial effects of the fusion of terminal polymerogenic units such as pyrrole and/or thiophene onto a central ring, properly tuned from the electronic point of view, for improving the characteristics of conductive polyheteroaromatics for practical applications. A further advantage of monomers 2, 3, 6 and 7 is associated with the possibility of their functionalization at a position remote from the polymerization site. Results of the research under way will be reported elsewhere.

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